I. C. 6486 MAY, 1931

DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
SCOTT TURNER, DIRECTOR

## INFORMATION CIRCULAR

# THE SIGNIFICANCE OF SOLVENT ANALYSIS AS APPLIED TO COAL

RECEIVED
JUN 15 1931
O. S. U. LIBRARY

BY

E. B. KESTER

I.C.6486,
May, 1931.

INFORMATION CIRCULAR

DEPARTMENT OF COMMERCE - BUREAU OF MINES

# THE SIGNIFICANCE OF SOLVENT ANALYSIS AS APPLIED TO COAL[1]

By E. B. Kester[2]

Of the many angles from which coal can be studied it is evident that some have a direct and others have only an indirect bearing on its physical or chemical nature. The more drastic the treatment employed in an investigation, the more inferential become the conclusions permissible from the experimental evidence obtained. Thus, ultimate and proximate analyses tell something concerning age, behavior on carbonization, and possible industrial usefulness, but nothing regarding structure or composition in the larger sense. Strong oxidation reveals the fact that benzenoid, pyrrol, and furane rings are prevalent in the chemical substances present, and milder oxidation indicates that the mass of coal, as in the case of the peats and lignites, is humic in character. But beyond such points of information, very little additional can be gained by the use of these more or less vigorous measures.

To gain wider knowledge of the actual constituents of coal substance as found investigators have worked out systems of separation by means of solvents, of which a large number have been employed at various times both singly and in combination. The list of solvents includes petroleum ether, benzene, toluene, xylene, ethyl ether, alcohol, acetone, carbon bisulphide, pyridine, quinoline, aniline, phenol, tetralin, glycol ethyl ether glycol ethyl-ether acetate, glycol methyl ether, glycol diethyl ether, pine oil, mesityl oxide furfural, benzaldehyde, ethylene oxide, rosin, caustic potash in solvents, amyl alcohol plus pyridine, chloroform, carbon tetrachloride, acetylene tetrachloride, naphthalene, and others.

Once a coal has been extracted it has become common practice to subdivide the extract by means of partial solution in other and weaker solvents. Thus, we find the oily and solid bitumens of Fischer (1),[3] Bone (2) and others; the alpha, beta and gamma constituents of Wheeler (3); the classification of Novak and Hubacek (4) embracing oils, resins A, resins B, bitumens An, bitumens Bn, and bitumens Cn; Crussard's (5) malthenes, asphaltenes, and carbenes, borrowed from asphalt terminology; and the 40 or more subdivisions of the phenol extract of coal worked out by Frazer and Hoffman (6).

Perhaps the primary object of interest in these many researches has been to find the coking principle of coal, and to study it and to learn why certain coals form hard, well-fused cokes, and others merely fall to pieces during carbonization. The origin of the various constituents of the gas and tar, the temperature at which each forms, and something of the mechanism of their synthesis have also been sought, as well as new bases for adjudging rank.

---

[1] The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6486."

[2] Senior organic chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

[3] Figures in parentheses refer to the bibliography at the end of this circular.

These attempts to classify the ingredients of coal by means of such relatively mild separations as are obtained by solvent extraction yield information which in the end is more fundamentally sound than data given by carbonization and by proximate and ultimate analyses, for as previously implied the latter are related in part only to the exceedingly complex structure comprising the coal substance. Their technical significance, however, can not be discounted.

The results of one research have given rise to controversy on occasion when in conflict with the findings of another, particularly where the conditions of test show variation. Certain inexplicable facts present themselves, such as the solubility of different coal ingredients before and after isolation from the parent coal and the stability of certain bitumens in solution under conditions that would result in their decomposition, were they isolated. The possible reciprocal effect of one class of substances upon another during the coking process has been ignored in many instances. Little work has been done toward isolation and identification of pure compounds extracted from coal, except in the case of a few hydrocarbons of relatively high molecular weight (8). However, the ultimate composition of coals both whole and subdivided has been determined by several investigators for purposes of comparison, although the information gleaned has not served to interpret behavior adequately, The role of the extracts in the coking process and in many instances the character and identity of the volatile products have been studied extensively. The behavior of the extracts under conditions of gradually rising temperature has been observed; that is, the physical evidence has been studied, such as melting points in the case of solids, range of stability, points of decomposition and of intumescence, and so on. Agglutinating values for different portions of coal extract have been determined.

## EXTRACTION BY BENZENE UNDER PRESSURE

The comprehensive work of Fischer (1) and associates is based on the pressure extraction of coal with benzene, followed by a separation of the extract with petroleum ether. By this means two distinct classes of compounds are obtained, termed the "oily" and the "solid" bitumens. By coking each in turn with the extracted coal it was found that the cohesiveness of the button was due largely to the oily bitumens, while the swelling (intumescence) could be ascribed to the solid bitumens. Fischer brings out the importance of both quality and amount of extractable bitumens. The noncoking coals, for example, yielded an extract that could be pulverized easily, whereas the coking coals yielded soft extracts because of the presence of a significant amount of oily bitumen of which he fixed at 0.5 per cent the minimum amount required for coking. It was proposed to use the information obtained from such experiments as an aid in coal blending. The properties of the original coal, he found, could be restored, more or less, by reincorporating the extracts with the extracted substance, and the behavior of a noncoking coal on carbonization could be reversed by relieving it of its impotent bitumens and uniting the residual substance with the extract of a strongly coking coal. The importance of the decomposition point of the solid bitumens is brought out. No swelling is produced where this occurs before the plastic state is reached. At the other extreme - that is, a too high decomposition point of solid bitumen - the gases liberated meet only a hard inflexible mass. Where a well-fused swollen coke is obtained this decomposition occurs within the plastic range. Bone (2) and coworkers conducted an investigation along somewhat similar lines but arrived at different conclusions. The coking power of coal, they found, resided largely in the portion of the extract corresponding to Fischer's solid bitumens; the softer, more soluble fractions contributed little to the coking process, although they were not without influence. Davis and Reynolds (9) confirmed their findings and described a third type of extractable substance which they call insoluble bitumen. In Fischer's laboratory Broche and Bahr (10) then proceeded to carry out additional experiments and included in parallel a series after Bone's method, which differed from Fischer's mainly in the use of powdered coke in place of extracted coal in the determination of agglutinating value. In the end, much the same conclusions were reached as before; in addition, Bone's experimental results were also confirmed. Obviously, both groups of investigators could not be correct; and to explain away their differences Broche and Bahr maintained with some justification that the behavior of a bitumen when carbonized with powdered coke is hardly typical of its behavior in the original coal, where the unextractable matter is by no means inert to pyrolysis.

Another point of difference, however, was not accounted for so easily. Bone himself had run a few agglutination tests, using extracted coal instead of powdered coke, and had obtained no intumescence with his "Fraction IV" which was the least soluble part of the solid extract. Here, indeed, was a result diametrically opposed to Fischer's. By way of explanation, the German authors offered the influence of particle size in the agglutinating test, stating that if the granules are too small the pores and capillaries are too few and poorly developed to hold the added extract firmly. In consequence, the extract distills rapidly away without exerting any binding action. Tests that illustrate this effect are described.

Another point of dissimilarity mentioned, probably an important factor, lies in the two methods of coking. Bone used a 10-gram sample supporting a 100-gram weight in a cylindrical vessel heated in an oven, whereas Fischer used only 1.5 grams heated in a platinum crucible over a burner.

Crussard (5) has emphasized the importance of impregnation as opposed to mere mixing in reconstructing a coal from the extract and extracted matter and has shown that the results of an agglutinating test are to some extent a function of the degree of impregnation. Lierg's experience (18), noted elsewhere in this paper, also can be cited in this connection. Crussard believes that the most useful agglutinants are the asphaltenes (corresponding to Fischer's solid bitumens) and quotes Lierg's law: "When bituminous substances of the same origin are arranged in a series of decreasing solubility, they are arranged in a series of increasing agglutinating power." Thus, in Bone's experiments with mixtures, the malthenes failed completely, giving a barely coherent coke, whereas the asphaltenes gave a well-agglomerated button. If the less soluble asphaltene was then fractionated further into true asphaltene and carbene, the still more insoluble carbene produced a still stronger and better coke.

## EXTRACTION WITH PYRIDINE

The Wheeler school (3) makes use of the extraordinary powers of pyridine to resolve coal into its soluble and insoluble portions. The extract is then fractionated further by partial solution in chloroform, and in this way are obtained what are called the alpha, beta, and gamma constituents. The first, the alpha, the portion of the coal not acted upon by pyridine, consists of resistant plant remains, high molecular-weight ulmines, and fusain; the beta is the portion removed by the pyridine but left behind by the chloroform. It consists mainly of dispersable ulmins of low molecular weight and resembles the alpha in many particulars, as will be shown. Finally, the gamma is the portion soluble in both pyridine and chloroform and is composed of resins and hydrocarbons. That it is truly resinic in character and related to common resins was shown by W. J. Russell (11), who studied the action of both on a photographic plate. It corresponds closely to the bitumens of Fischer, Bone, and others. Chiefly, in it reside the coking powers of coal.

That the alpha and beta constituents are of a nature chemically similar may be seen from comparison of their proximate and ultimate analyses and an examination of the volatile products of pyrolysis. Clark and Wheeler (12) resolved a coal in the above manner and made the following analyses of the different portions of extract.

Analyses of Alpha, Beta, and Gamma Constituents, Per Cent
(Clark and Wheeler)

| | Pyridine insoluble; alpha | Pyridine soluble, chloroform insoluble; beta | Pyridine soluble, chloroform soluble; gamma |
|---|---|---|---|
| Volatile matter | 34.96 | 31.88 | 77.33 |
| Fixed carbon | 65.04 | 68.12 | 22.67 |
| Carbon | 80.81 | 77.32 | 85.33 |
| Hydrogen | 5.23 | 5.14 | 7.08 |
| Oxygen | 10.40 | 14.26 | 4.56 |
| Nitrogen | 2.14 | 2.07 | 1.71 |
| Sulphur | 1.42 | 1.21 | 1.32 |

The yield of volatile products produced at carbonization temperatures ranging from 600 to 1000° C. has been worked out for each, and the constituents of the gas determined. Comparison of the data obtained on carbonization at 1000° is included here.

Carbonization of Alpha, Beta, and Gamma Constituents
(Carbonization at 1000° C.)

| | Alpha | Beta | Gamma |
|---|---|---|---|
| Total volatile matter | 37.7 | 38.6 | 78.2 |
| Tar | 3.8 | 9.0 | 42.9 |
| Gas, cubic centimeters per gram | 417.1 | 381.8 | 221.6 |
| Gas analysis, per cent: | | | |
| Carbon dioxide | 5.35 | 5.15 | 4.65 |
| Unsaturates | .80 | 1.00 | 8.60 |
| Carbon monoxide | 30.80 | 26.80 | 10.60 |
| Hydrogen | 44.90 | 47.45 | 39.50 |
| Methane | 11.65 | 14.05 | 31.90 |
| Ethane and other paraffins | 2.35 | 2.05 | 3.50 |
| Nitrogen | 4.15 | 3.50 | 1.25 |

The similarity between the amounts of each gas from the alpha and from the beta is evident. The hydrocarbons liberated from the gamma, it will be observed, greatly exceed the amount from either the alpha or the beta. On the other hand, the hydrogen from the alpha or the beta is greater than that from the gamma. Jones and Wheeler (3) have reported the very striking instance of a bituminous Durham coal in which no hydrogen at all was liberated from the gamma, while 14.8 and 19.1 per cent, respectively, was present in the gases from the alpha and the beta. The carbonization, however, was carried out below 450° C.

The residue from either a high or low temperature carbonization of the alpha and the beta compounds shows that no fusion effects have taken place, while the gamma yields a well-fused, pitchlike mass, and if the carbonization is carried out below 450° the residue is completely soluble in pyridine.

The distillation of alpha and of beta constituents at low temperatures yielded comparatively small amounts of liquid products (3) containing a large proportion of phenols, the remainder being principally water and hydrocarbons. The gamma generated considerable amounts of liquid hydrocarbons but no phenols. What few oxygenated compounds were present in either were not of an alcoholic nature, as was evidenced by treating the oils with metallic sodium.

The similarity of the alpha to the beta was corroborated further by Pearson (13), who treated a series of samples of each with fuming sulphuric acid at different temperatures over varying periods of time, obtaining as products what he called "oxahumins". The behavior of the original substances, as evidenced by the similarity in the progressive changes in the ultimate analyses under more and more drastic treatment, brings out a strong resemblance. An interesting sidelight in this study is the remarkable stability of the nitrogen that occurs in these bodies. This fact has also been observed by Oswald and Pinta (14), who studied the changes in the ultimate analysis of coals on continued oxidation.

A number of other investigators had observed the effect on its coking properties of extracting coal with pyridine. Anderson and Henderson (15) showed that if coal is extracted with pyridine the residual material undergoes a decided change in its coking properties. Weakly coking coals are rendered noncoking, whereas those with strongly coking characteristics are weakened in this respect. Wahl (16) extracted a number of coals with pyridine and found that the action of this solvent modified the appearance of the coke greatly and that the latter was more compact, darker, and considerably less voluminous than the coke from unextracted coal. Bone (17) carbonized the chloroform-soluble portion of the pyridine extract (the gamma) with powdered coke in the proportions of 1 to 9 and obtained a well-fused button, whereas the insoluble portion yielded only a pulverulent residue. Lierg (18) extracted a Karwin coal with pyridine and obtained 30 per cent by weight of extract. He found that if this was returned to the extracted matter in the form of a fine powder the mixture did not agglomerate on heating. Baker (19), in his investigations of three different coals, found that the coking property of two was destroyed completely by the solvent action of pyridine, while that of the third was practically destroyed. Pearson (13) observed that if coking tests were made on the alpha or the beta compounds while still retaining much adsorbed pyridine all of the beta yielded strong cokes, as did the alpha also when isolated from strongly coking coals; but if either was heated until the pyridine was expelled its coking powers deteriorated considerably and in some instances were completely destroyed.

Harger (20), who extracted coal with pyridine under pressure at 160 to 180° C., believes that the process is not a case of ordinary solution and that there appears to be some kind of simplification in the structure of the constituents which yields the pyridine-soluble matter. Probably, an effect similar to depolymerization is produced. In support of this contention it may be stated that the extract removed from the coal direct by means of chloroform contains neither nitrogen nor sulphur, whereas the chloroform-soluble part of the pyridine extract contains both these elements.

It is unfortunate that a complete separation of the gamma compounds from the remainder of the coal can not be made by direct extraction with chloroform, but attempts to do so have yielded only small quantities of soluble hydrocarbons and resins, whereas, by extracting the same coal first with pyridine and then the pyridine extract with chloroform, much larger quantities of soluble substance are obtained. This characteristic of pyridine, together with the difficulty of removing completely all traces of it from both extract and residue, confirms the previous postulate that pyridine performs rather more than a solvent action on the coal substance. Crussard (5) speaks of pyridine as being capricious in its action; that is, one experiences difficulty in obtaining identical amounts of extract on split samples. The variation is probably in the beta constituent, as the same amounts of gamma are removed by quinoline, with its high boiling point, as by pyridine. In one of Bone's earlier papers (21) he describes the precautions and precise detail necessary for accurate extraction with pyridine, emphasizing the importance of rigid exclusion of air and moisture. In spite of extreme care, however, four extractions yielded amounts of material ranging from 30.44 to 32.48 per cent. It is something of a problem to account for these wide differences when the extractions were carried out under conditions so well controlled.

Errors other than those due to moisture and oxidizing influences are possible. The caking and swelling effect which pyridine has on finely divided coal is one that even protracted extraction may not overcome, and the difficulty of removing all the pyridine from its extract may be another. The first may be taken care of by choosing a small enough sample and diluting it in the Soxhlet thimble with several volumes of clean sand.

As for the second, the problem of getting rid of all the pyridine, which has been an annoyance to every investigator who has extracted coal with this solvent, is difficult. Even washing with strong mineral acids does not remove it entirely. The formation of a molecular complex with some of the coal substance has been suggested by way of explanation. Another, that of Pearson (13), is based upon the assumption that pyridine dissolves only the resinic portions of coal and that the other coal substances apparently dissolved by it are of humic origin and are merely dispersed as colloidal aggregates. To support this attitude he cites the following facts on the difficult removal of pyridine from the extract:

1. That the humic matter or "ultrahumins", as he calls them, when isolated retain pyridine tenaciously, although in amounts that vary continuously with the conditions. It is removable in a vacuum at a slow but continuous rate.

2. That if the ultrahumins are placed in contact with another solvent the adsorbed pyridine passes into solution, and its place is taken by the new solvent on the surface of the ultrahumins.

3. That when the pyridine is finally removed in toto in a vacuum steam oven only 10 per cent of the ultrahumins can be redispersed in the pyridine, a behavior characteristic of an irreversible colloid.

Original from THE OHIO STATE UNIVERSITY

The use of xylene to remove the pyridine has recently been demonstrated (22). Specifically, if the pyridine solution of extract is evaporated to a small volume the remainder can be driven off completely by adding increments of this solvent and distilling to a low volume after each addition and finally to dryness under reduced pressure. The xylene, held far less tenaciously than the pyridine, can then be removed completely in a vacuum desiccator over paraffin shavings and concentrated sulphuric acid. After this treatment no trace of pyridine odor is perceptible. No treatment with strong mineral acids is necessary. When this procedure is followed it is usually possible to obtain results on duplicate samples differing by less than 1 per cent.

To resolve the gamma extract still further Cockram and Wheeler (23) treated it successively with light petroleum, ethyl ether, and acetone and so obtained gamma$_1$, gamma$_2$, gamma$_3$, and gamma$_4$, in the order of their isolation by these solvents, the gamma$_4$ representing the residuum insoluble in acetone. A table illustrating the differences in ultimate analysis of the gamma subdivisions of a Parkgate clarain is included for purposes of comparison.

Ultimate Analysis of Gamma Subdivisions of Parkgate Clarain

| | Per cent of total gamma | Per cent of coal | Per cent | | | |
|---|---|---|---|---|---|---|
| | | | C | H | S | O + N |
| Gamma$_1$ | 33 | 2.30 | 83.90 | 9.00 | 0.74 | 6.36 |
| Gamma$_2$ | 37 | 2.54 | 82.72 | 6.90 | .91 | 9.47 |
| Gamma$_3$ | 12 | .83 | 79.00 | 5.70 | .89 | 14.41 |
| Gamma$_4$ | 18 | 1.23 | 80.00 | 5.90 | 1.10 | 13.00 |

Gamma$_1$ was of vaselinelike consistency and comprised 40 per cent of saturated hydrocarbons, 40 per cent of unsaturated hydrocarbons, and 20 per cent of resins.

Gamma$_2$ was a brick-red powder containing 15 per cent of saponifiable matter, the acids liberated in the saponification consisting of phenols and carboxylic acids, some of which possessed hydroxy groups. The unsaponifiable portion contained 8.8 per cent of oxygen, present as bridge-linkages.

Gamma$_3$ and gamma$_4$ were brown powders similar to one another in general properties and composition. Both were insoluble in alcoholic potash.

Destructive distillation of each in vacuo up to 600° C. brought out striking differences, as follows:

Result of Destructive Distillation of Gamma Constituents

| | Volatile matter, per cent | Tar and oil, per cent | Gas, c. c. per gram |
|---|---|---|---|
| Gamma$_1$ | 100.0 | Distilled unchanged below 300° | |
| Gamma$_2$ | 61.7 | 46.0 | 96.6 |
| Gamma$_3$ | 48.3 | 13.0 | 140.5 |
| Gamma$_4$ | 41.0 | 16.7 | 185.0 |

The tars from $\text{gamma}_2$ distilled between 200 and 300° C. for the most part and consisted almost entirely of hydrocarbons. The residue was a dark brown, lustrous intumescent mass insoluble in chloroform. $\text{Gamma}_3$ and $\text{gamma}_4$ produced tars containing small amounts of phenols; the gases resembled those from the beta. A table showing comparative gas analyses follows.

Comparative Analyses of Gas from Destructive Distillation of Gamma Constituents, Per Cent

| Constituent | $\text{Gamma}_2$ | $\text{Gamma}_3$ | $\text{Gamma}_4$ |
|---|---|---|---|
| Carbon dioxide | 5.2 | 5.7 | 6.2 |
| Higher olefins | 2.0 | 2.1 | 2.3 |
| Ethylene | 1.0 | 1.0 | 1.7 |
| Carbon monoxide | 6.5 | 6.8 | 9.5 |
| Hydrogen | 32.5 | 62.7 | 52.0 |
| Paraffins | 54.4 | 21.7 | 28.2 |

A decided break in the gas analysis between $\text{gamma}_2$ and $\text{gamma}_3$ is observable; that is, the order of prominence of hydrogen and paraffins is reversed, the new order reappearing in $\text{gamma}_4$. The other gases show no marked variation.

$\text{Gamma}_3$ and $\text{gamma}_4$ may therefore be looked upon in the light of transition compounds between the true resins and the beta compounds which have an ulmic character. The foregoing table relates them to the beta, but oxidation with 30-per cent nitric acid brings out differences. For example, the beta compounds are oxidizable in part to picric and benzene polycarboxylic acids by this reagent (9), while neither type of compound is formed from $\text{gamma}_3$ or $\text{gamma}_4$ under identical conditions. Also, the latter melt at temperatures no higher than many resin inclusions without decomposition, whereas no ulmins examined so far by these authors melt on heating; all decompose without fusing.

From coking tests Cockram and Wheeler concluded that the mere quantity of total gamma was not necessarily a measure of the quality of product, as the different subdivisions behaved differently in the test. Both $\text{gamma}_1$ and $\text{gamma}_2$ produced hard, well-fused buttons, but neither $\text{gamma}_3$ nor $\text{gamma}_4$ yielded coherent residues.

A comparison is made in this same paper between the different constituents of the gamma portion of coal and the benzene-pressure extract with which it is quite comparable both in kind and amount. The latter is resolved in the same manner as is the gamma. The following table brings out the points of similarity and difference.

Original from THE OHIO STATE UNIVERSITY

Comparison of Gamma Constituents and Benzene-Pressure Extracts, Per Cent of Ash-Free dry Coal
(Parkgate clarian)

| | Gamma constituents | Benzene-pressure extracts | |
|---|---|---|---|
| | | 200° C. | 285° C. |
| Soluble light petroleum | 2.30 | 2.22 | 2.55 |
| Hydrocarbons | C, 83.9; H, 9.0 | C, 85.0; H, 9.0 | C, 85.4; H, 9.2 |
| Soluble ether | 2.54 | 2.02 | 1.97 |
| Resins | C, 82.7; H, 6.9 | C, 84.0; H, 6.8 | C, 84.2; H, 7.3 |
| Insoluble ether | 2.06 | 1.72 | 2.78 |
| Resinlike substances | C, 79.5; H, 5.8 | C, 82.5; H, 5.6 | C, 79.4; H, 5.8 |

Undoubtedly there is a correlation here of the corresponding fractions. A series of coking tests would have borne out the similarity, but none are reported.

It is to be deplored that more comparisons of systems of solvent analysis have not been made. When an investigator isolates a fraction of coal extract by selective solution he is always in doubt as to whether he should regard it as an established entity of the coal substance or seek to resolve it further. If he could arrive by another route at the same quantity of product bearing the same analysis and possessing the same physical and chemical properties he would feel reassured that he had actually isolated a more or less definite class of compounds.

Bone (21) has attempted to find a relation between the amount of material extractable with pyridine and the volatile matter in the coal but concluded from comparison of the results for two coals that there was no relationship. For example, Durham coal, extractable to the extent of 30 to 32 per cent, had a volatile-matter content of 26.3 per cent; and Barnsley coal, 11.6-per cent extractable, had 32.2 per cent of volatile matter. The ratio of carbon to hydrogen in the extract of the Durham he found decidedly lower than that in the unextracted coal, whereas the residue was correspondingly higher in this respect. Thus, in the dry coal, the carbon:hydrogen ratio was 17.60; in the residue, 19.12; and in the pyridine extract, 13.44.

Bone also compared the amounts of extract obtainable with pyridine and the homologous picolines boiling 130 to 150° C. and found that approximately the same quantity of material was abstracted. On the other hand, if the extraction was carried out with pyridine 130 to 150° under pressure more than double the quantity of extract was obtained. Oxygen was found to have a retarding effect on the rate of extraction.

## EXTRACTION WITH PHENOL

The use of phenol as a partial solvent for coal, introduced by Guignet (24), was studied at greater length by Frazer and Hoffman (6), who had discovered after trying a number of organic reagents that pyridine, aniline, and phenol removed the largest amount of soluble material. By means of phenol they were able to extract 10.87 per cent of a noncoking bituminous coal from Franklin County, Ill. After freeing the extract of the solvent they proceeded to subdivide it by using other and weaker solvents, such as ether, acetic acid, methanol, acetone, benzene, and petroleum ether. The several specimens obtained showed varying physical properties, and some even gave evidence of being more or less pure chemical substances. The authors concluded from their research that for lack of evidence to the contrary these substances existed as such in the coal before extraction.

Parr and Hadley (25) extracted two Illinois coals with plenol at 110° C. and reported that the coals lost their coking properties by this treatment. Both extract and residue tended to oxidize at room temperature and had an avidity for water. The ultimate analysis of the original coals and the corresponding extracts and residues were approximately the same, although the extracts yielded the more volatile matter on distillation. According to these authors neither residue nor extract produced on carbonization what could properly be called a coke. The extract yielded only a friable mass, whereas the residue showed no evidence whatever of fusion; yet the unextracted coal had good coking properties, and it was found possible to restore this condition by reuniting the extract with the residue. Here is an outstanding example of reciprocal effect.

Parr and Hadley compared the gases yielded by both extract and residue. From the following table it is evident that the yields of hydrogen and hydrocarbons do not follow at all the results of Wheeler and associates. In fact, they are exactly the reverse, if the material extractable with phenol is at all comparable with that extractable with pyridine; that is, instead of the extract yielding a lower ratio of hydrogen to paraffins than the residue, the opposite is true. Either the materials extractable by these two solvents are not similar or the coals are sufficiently different to show this reversed effect when both are extracted with the identical solvent. The illustration brings out the impossibility of generalizing as to the absolute properties of either extract or residue.

Components of Gases by Destructive Distillation, Per Cent

| Constituent | Vermillion County Coal | | | Williamson County Coal | | |
|---|---|---|---|---|---|---|
| | Original | Residue from phenol extraction | Phenol extract | Original | Residue from phenol extraction | Phenol extract |
| Carbon dioxide | 18.1 | 15.1 | 12.9 | 7.1 | 6.9 | 7.2 |
| Ethylene | 3.4 | 3.5 | 3.1 | 3.1 | 2.9 | 2.6 |
| Oxygen | .5 | .9 | .1 | .6 | .8 | .7 |
| Carbon monoxide | 20.6 | 17.4 | 16.4 | 12.8 | 16.5 | 11.8 |
| Hydrogen | 35.6 | 39.2 | 47.8 | 50.7 | 46.0 | 51.8 |
| Methane | 17.4 | 18.1 | 13.4 | 17.3 | 20.5 | 18.2 |
| Ethane | 1.6 | 1.5 | 2.8 | 1.9 | 2.8 | 2.7 |
| Nitrogen | 2.8 | 4.3 | 3.5 | 6.5 | 3.6 | 5.0 |

The most important conclusions drawn by Parr and Hadley were:

1. That coking coals from Vermillion, Madison, Montgomery and Williamson Counties when extracted with phenol all yielded noncoking residues.

Original from THE OHIO STATE UNIVERSITY

2. That both extract and residue absorbed moisture and carbon dioxide readily.

3. That the extract contained more volatile matter than the residue.

4. That oxidation of both the residue and the extract lowers the percentage of volatile matter in each.

5. That if the oxidation is applied to the coal the amount of extractable matter and the coking properties of the coal are lowered and that there is an increased carbon dioxide content of the gases produced by thermal decomposition.

## EXTRACTION WITH TETRALIN

Perhaps the most exhaustive effort in the field of solvent analysis has been that of Novak and Hubacek (4). It is exhaustive in the sense that each of the tetralin extracts of a series of four coals ranging from lignite to full bituminous has been subdivided into six portions and that determinations have been made of the proportions on the basis of both the total extract and the whole coal, the ultimate and the proximate analyses, the influence on the coking powers of the coal, and the relative amounts of volatile matter liberated between certain temperature limits. The last, together with the melting points, is taken as a measure of thermal stability. The six classes of substances isolated by them may be described briefly as follows:

1. Oils.- Portion of the tetralin pressure extract soluble both in benzene and petroleum ether.

2. Resins A.- Portion of the tetralin pressure extract soluble in benzene but not in petroleum ether.

3. Resins B.- Portion of the tetralin pressure extract precipitated from benzene solution by addition of petroleum ether; soluble in alcohol.

4. Bitumens An.- Portion of the tetralin pressure extract precipitated from benzene solution by addition of petroleum ether; insoluble in alcohol.

5. Bitumens Bn.- Portion of the tetralin pressure extract insoluble in benzene.

6. Bitumens Cn.- Portion of the coal insoluble in tetralin but soluble in pyridine.

To avoid reprinting the large number of tables which bring out many interesting comparisons only the most important generalizations established will be noted:

1. The content of oils is highest in the case of the lowest-rank coal, the Karolina, the amount diminishing steadily from its high value of 32 per cent through the series until it is only 11 per cent of the extract in the case of the bituminous Jaroslav. On the basis of the ash-free dry coal this represents a drop from 8 to 2 per cent.

2. The resins follow the same order as the oils.

3. The bitumens and particularly bitumens Bn are highest in the bituminous coal, amounting to 66⅔ per cent of the extract of the Jaroslav, but only 25 per cent of the Karolina extract.

4. Bitumens An, the next stage of insolubility beyond the resins, are quite different in character from the latter, having no resin odor and melting considerably higher. The carbon content is 2 to 3 per cent lower and the oxygen higher than those of resins B.

5. The benzene-insoluble portion was completely souble in pyridine.

6. Progressive changes are not always present in the series. For example, the carbon content of bitumens Bn from the subbituminous Max in relation to the brown Hedvika and the bituminous Jaroslav is higher than that from either. Also, the melting point is higher.

7. The coking power of the Jaroslav was not lost after an 8-hour pressure extraction with tetralin but was removed completely if the residue was extracted further with pyridine.

8. The pyridine extract, bitumens Cn, from both the bituminous and subbituminous coals yielded on carbonization a highly swollen and coherent residuum, whereas the pyridine extract of the brown coals did not coke.

9. It is doubtful whether bitumens Cn on account of the manner of isolation are true bitumens or merely mixtures of the more difficultly soluble bitumens Bn with coal ulmins. Very probably these are related to gamma$_3$ and gamma$_4$ of Cockram and Wheeler, which are semiulmic in character. The material isolated from the brown Karolina would not melt at all, while that from the subbituminous Max and the bituminous Jaroslav merely became plastic.

In part 2, these authors take up the agglutinating powers of the several portions of extract. Powdered coke was used in these tests mixed with the proper proportions of extract. The following generalizations were drawn:

1. The most swollen cokes were obtained where the inert material was a minimum, while the hardest resulted from ratios of inert to substance of 3:1.

2. Carbonization of the bitumens alone resulted in highly swollen cokes, but the resins yielded barely coherent residues.

3. All extractable substances having a more or less distinct melting point are able to bind the inert material to some extent; even the liquid substances from the noncoking or brown coals were by no means devoid of this property.

4. The amount of "cementing residuum" left after carbonization is important. Agglutinating power is attributed to those fractions which on coking leave a relatively large amount of cemented residuum that has fused and hardened. The oils, for example, representing 3.3 to 8.3 per cent of the coal substance, yielded less than 4 per cent of its own weight of fixed carbon. Therefore, its cementing residuum would be negligible. Resins A behaved similarly.

5. Bitumens Bn appear to be the most important factor affecting the agglutinating power, as the following table based upon the percentage of original coal appearing as cementing residuum will show.

Cementing Residuum, Percentage of Original Coal
(Ash-free dry-coal basis)

|  | Resins |  | Bitumens |  |  |  |
|---|---|---|---|---|---|---|
| Coal | A | B | An | Bn | Cn | Total |
| Karolina | 0.55 | 0.77 | 0.80 | 2.18 | — | 4.6 |
| Hedvika | .43 | .44 | .90 | 3.77 | — | 5.84 |
| Max | — | .45 | .79 | 11.72 | 7.40 | 20.66 |
| Jaroslav | — | .44 | .51 | 12.45 | 5.82 | 20.52 |

The amount of bitumens Bn, however, is not the only factor governing coking. Its thermal stability is another. For example, Max and Jaroslav yield about the same amount of Bn, but the one is coking and the other noncoking. Also, the thermal stability of the other constituents of the extract may ameliorate or lessen its powers according to their individual stabilities. The term "thermal stability" is defined as the range of temperature during which a certain constituent remains liquid, semisolid, or plastic before it solidifies because of loss of volatile matter evolved on further heating. If this is small, on the order of 20 to 30°, rapid decomposition and fast solidification set in, yielding either no coke or one of poor quality. If it is high - that is, above 120° C. - the coke is of excellent quality.

Thermal stability was measured by fractional coking tests similar to those used by Illingworth (26). One gram of sample overlaid with infusorial earth and surmounted with a glass plunger was raised in a 2-hour period to 300° C. and maintained there 1 hour. It was cooled and weighed, the loss of volatile matter was recorded, and it was again placed in the muffle preheated to 300°. During a period of 2 hours the temperature was now raised to 350°, and so on at 50° stages to 450 or 500° C.; the losses in weight at each step were noted.

Fractional Decomposition of Bitumens Bn

| Temperature range, °C. | Per cent volatile matter of Bn lost Karolina | Hedvika | Max | Jaroslav |
|---|---|---|---|---|
| To 300 | 9.13 | 1.67 | 2.56 | 1.01 |
| 300-350 | 6.78 | 11.89 | 8.18 | 6.08 |
| 350-400 | 22.00 | 21.70 | 19.96 | 13.68 |
| 400-450 | 12.06 | 17.18 | 16.38 | 14.46 |

By means of curves the authors calculated the range over which the bitumen remains in the liquid or plastic state and concluded that this value for the Jaroslav bitumens Bn is about 120° (326-446) while the corresponding range for the Max is only about 30° (370-400). Fractional coking of the other constituents of the extract is reported in separate tables, with a view of bringing out either their favorable or adverse influences in the coking powers that reside chiefly in bitumens Bn, but the evidence is not altogether conclusive.

In general, it is noticeable on totaling the fractional losses of volatile matter that the volatile matter evolved at all temperature intervals is higher for the non coking Max than the coking Jaroslav.

## CONCLUSION

The impression gained from a survey of the work accomplished up to the present on the solvent analysis of coal is that there is a decided lack of unity and standardization throughout the field. A fair comparison of systems is almost impossible, as wide variations are found in the kinds of coal examined, angles of inquiry, conditions of individual tests, and bases of statistical data. Undoubtedly overlapping of efforts has occurred repeatedly, and many irreconcilable facts remain quite unexplained.

Again, comparatively little stress has been laid on correlation of coal extracts with properties of the parent substance other than its coking properties. In the survey of the gas, coke, and by-product making properties of American coals now being conducted at the Pittsburgh Experiment Station of the United States Bureau of Mines an exhaustive and comprehensive study is being made of a large number of coals varying in age and geographic location. Included among the many individual tests carried out are determinations of the oily, solid, and insoluble bitumens from the benzene-pressure extraction, the alpha, beta, and gamma constituents, and the "rational-analysis" classification originally proposed by Cockram and Wheeler (23) and later amplified by Francis and Wheeler (27). The last-mentioned, while not pertaining strictly to solvent extraction, is related closely enough to be mentioned here. It involves separation of the coal into its three normal constituents, the resins and hydrocarbons (estractable with solvents), the ulmins and the resistant plant remains, and a determination of the respective amounts of each. The ulmins are removed from the coal (freed of resins and hydrocarbons) by an oxidation process with nitric acid and potassium chlorate, which "regenerates" the humic acids from which they originated and permits their separation from the third type of substance, the resistant plant remains by an alkaline extraction.

Digitized by Google Original from THE OHIO STATE UNIVERSITY

An additional factor included in rational analysis is the "reactivity index". Originally the reactivity of a coal toward oxidizing agents was taken as the length of time required to convert half the ulmins present to humic acids under controlled conditions of atmospheric oxidation. However, the operation was too lengthy and involved, requiring weeks of time and frequent withdrawals of test samples. Francis and Wheeler substituted a chemical method of oxidation and the term "reactivity index" as a measure of susceptibility to oxidizing influences. It is determined by digesting a ½-gram sample of coal in a sealed container with 50 c. c. of normal hydrochloric acid and 0.5 gram of potassium chlorate for 6 hours at water-bath temperature, and ascertaining the loss after extracting the oxidized coal with caustic potash. It is claimed that the figures obtained by this method serve to align the coals in substantially the same order as the longer air-oxidation process. It has been our experience at Pittsburgh that the coals studied to date in this connection possess reactivity indexes that follow differences in their carbon content fairly well in the reverse order.

No attempt has been made yet to correlate the rational and solvent analyses with the results of other tests; but in due time, when complete tabulations have been made, it will be possible to advance interpretations.

A separate study merely to correlate systems of solvent analysis carried out on a single coal, which would include an exhaustive study of fractional extracts produced in a variety of ways, would also be of value. Possibly no exact separations can ever by made of classes of coal substance so intimately bound together because of the very evident shading of one class into another, but it is to be hoped that the result of such a work would be the recommendation of a master system of practical usefulness and of material assistance in fundamental studies.

## BIBLIOGRAPHY

1. Fischer, F., Broche, H., and Strauch, J. The Constituents of Bitumens from Bituminous Coal and Their Influence on Coking and Swelling Properties. Brennstoff-Chem., vol. 5, 1924, p. 299; vol. 6, 1925, p. 33.

2. Bone, W. A., Pearson, A. R., and Quarendon, R. Researches on the Chemistry of Coal. III, Extraction of Coal by Benzene under Pressure. Proc. Roy. Soc., vol. 105A, 1924, p. 608; Bone, W. A., Horton, L., and Tei, L. J. Researches on the Chemistry of Coal. V, The Maturing of Coal Considered from the Standpoint of Its Benzene-Pressure Extract. Proc. Roy. Soc., vol. 120A, 1928, p. 523.

3. Jones, D. T., and Wheeler, R. V. The Composition of Coal. Jour. Chem. Soc., vol. 107, 1915, pp. 1318-24; Constitution of Coal, same, vol. 109, 1916, pp. 707-14; Stopes, M., and Wheeler, R. V. The Constitution of Coal. Dept. Sci. and Ind. Res., p. 41.

4. Novak, H., and Hubacek, J. The Fractionation of Coal with Solvents, and the Influence of the Soluble Portion upon the Agglutinating Power of Coal. Paliva Topeni, vol. 10, 1928, pp. 3-9, 22-8, 28-33, 41-51.

5. Crussard, M. L. The Agglutination of Coal. Fuel, vol. 9, 1930, p. 177.

6. Frazer, J. C. W., and Hoffman, E. J. The Constituents of Coal Soluble in Phenol. Tech. Paper 5, Bureau of Mines, 1912, 18 pp.

7. Francis, W., and Wheeler, R. V. Resins in Coal—Studies in the Composition of Coal. Jour. Chem. Soc., vol. 127, 1925, p. 2236; same, 1926, p. 1410.

8. Hofmann, F., and Damm, P. Pyridine Extraction of Upper Silesian Bituminous Coal. Brennstoff Chem., vol. 3, 1922, pp. 73-79, 81-91; same, vol. 4, 1923, p. 65. Pictet, A., and Ramseyer, L. Arch. Sci. Phys. Nat., vol. 34, p. 234.

9. Davis, J. D., and Reynolds, D. A. Coking Constituents of Mesa Verde and Pittsburgh Coals. Ind. Eng. Chem., vol. 18, 1926, p. 838; Benzene-Pressure Extraction of Coals. Ind. Eng. Chem., vol. 21, 1929, p. 1295.

10. Broche, H., and Bahr, T. The Oily and Solid Bitumens of Coal. Brennstoff-Chem., vol. 6, 1925, p. 349.

11. Russell, W. J. Proc. Roy. Soc., vol. 80B, 1908, p. 376.

12. Clark, A. H., and Wheeler, R. V. The Volatile Constituents of Coal. Jour. Chem. Soc., vol. 102, 1913, p. 1704.

13. Pearson, A. R. Some New Derivatives of Bituminous Coal. Jour. Soc. Chem. Ind., vol. 42, 1923, 68-72.

14. Oswald, M. and Pinta, R. The Oxidation of Coals and Their Naphthalene Extracts. Chem. et Ind., vol. 13, 1925, p. 548.

15. Anderson, W. C. and Henderson, J. A. R. The Coals of Bengal and Japan. Jour. Soc. Chem. Ind., vol. 21, 1902, pp. 237-43.

16. Wahl, A. Researches on Coal. Soc. Ind. de l'Est. Bull. 100, 1912; Compt. rend., vol. 154, 1912, pp. 1094-1097.

17. Bone, W. A., Pearson, A. R., Sinkinson, E., and Stockings, W. E. Researches on the Chemistry of Coal: II. Resinic Constituents and Coking Properties of Coal. Proc. Roy. Soc., vol. 100A, 1922, pp. 582-598.

18. Lierg, F. Contributions to the Chemistry of the Coking Process. Zeit. angew. Chem., vol. 35, 1922, p. 164.

19. Baker, T. The Solvent Action of Pyridine on Certain Coals. Trans. Fed. Inst. Min. Eng., vol. 20, 1901, pp. 156-163.

20. Harger, J. Coal and the Chemistry of its Carbonization. Jour. Soc. Chem. Ind., vol. 33, 1914, pp. 389-392.

21. Bone, W. A., and Sarjant, R. J. Researches on the Chemistry of Coal: I. Action of Pyridine on Coal Substance. Proc. Roy. Soc., vol. 96A, 1919, pp. 119-136.

22. Kester, E. B., and Schneider, E. J. The Rational Analysis of Coal and Its Resolution into Alpha, Beta, and Gamma Constituents. Paper presented before Spring meeting, American Chemical Society, Indianapolis, Ind., 1931.

23. Cockram, C., and Wheeler, R. V. Studies in the Composition of Coal. The Resolution of Coal by Means of Solvents. Jour. Chem. Soc., 1927, pp. 700-718.

24. Guignet, E. The Constitution of Coal. Compt. rend., vol. 88, 1879, 590-592.

25. Parr, S. W., and Hadley, H. F. Analysis of Coal with Phenol as a Solvent. Univ. of Ill. Eng. Exp. Sta. Bull. 76, 1914.

26. Illingworth, S. R. Coal and Its Carbonization. Fuel, vol. 1, 1922, p. 34.

27. Francis, W., and Wheeler, R. V. Studies in the Composition of Coal. The Rational Analysis of Coal. Jour. Chem. Soc., 1928, pp. 2967-2979.